4.0 Application of Chemical Reaction Models

Computerized chemical reaction models based on thermodynamic principles may be used to calculate processes such as aqueous complexation, oxidation/reduction, adsorption/desorption, and mineral precipitation/dissolution for contaminants in soil-water systems. The capabilities of a chemical reaction model depend on the models incorporated into its computer code and the availability of thermodynamic and/or adsorption data for aqueous and mineral constituents of interest. Chemical reaction models, their utility to understanding the solution chemistry of contaminants, and the MINTEQA2 model in particular are described in detail in Chapter 5 of Volume I.

The MINTEQA2 computer code is an equilibrium chemical reaction model. It was developed with EPA funding by originally combining the mathematical structure of the MINEQL code with the thermodynamic database and geochemical attributes of the WATEQ3 code. The MINTEQA2 code includes submodels to calculate aqueous speciation/complexation, oxidation-reduction, gas-phase equilibria, solubility and saturation state (*i.e.*, saturation index), precipitation/dissolution of solid phases, and adsorption. The most current version of MINTEQA2 available from EPA is compiled to execute on a personal computer (PC) using the MS-DOS computer operating system. The MINTEQA2 software package includes PRODEFA2, a computer code used to create and modify input files for MINTEQA2.

The MINTEQA2 code contains an extensive thermodynamic database for modeling the speciation and solubility of contaminants and geologically significant constituents in low-temperature, soil-water systems. Of the contaminants selected for consideration in this project [chromium, cadmium, cesium, tritium (^{3}H), lead, plutonium, radon, strontium, thorium, and uranium], the MINTEQA2 thermodynamic database contains speciation and solubility reactions for chromium, including the valence states Cr(II), Cr(III), and Cr(VI); cadmium; lead; strontium; and uranium, including the valence states U(III), U(IV), U(V), and U(VI). Some of the thermodynamic data in the EPA version have been superseded in other users' databases by more recently published data.

The MINTEQA2 code includes 7 adsorption model options. The non-electrostatic adsorption models include the activity K_d^{act}, activity Langmuir, activity Freundlich, and ion exchange models. The electrostatic adsorption models include the diffuse layer, constant capacitance, and triple layer models. The MINTEQA2 code does not include an integrated database of adsorption constants and reactions for any of the 7 models. These data must be supplied by the user as part of the input file information.

Chemical reaction models, such as the MINTEQA2 code, cannot be used *a priori* to predict a partition coefficient, K_d, value. The MINTEQA2 code may be used to calculate the chemical changes that result in the aqueous phase from adsorption using the more data intensive, electrostatic adsorption models. The results of such calculations in turn can be used to back calculate a K_d value. The user however must make assumptions concerning the composition and mass of the dominant sorptive substrate, and supply the adsorption parameters for surface-complexation constants for the

contaminants of interest and the assumed sorptive phase. The EPA (EPA 1992, 1996) has used the MINTEQA2 model and this approach to estimate K_d values for several metals under a variety of geochemical conditions and metal concentrations to support several waste disposal issues. The EPA in its "Soil Screening Guidance" determined MINTEQA2-estimated K_d values for barium, beryllium, cadmium, Cr(III), Hg(II), nickel, silver, and zinc as a function of pH assuming adsorption on a fixed mass of iron oxide (EPA, 1996; RTI, 1994). The calculations assumed equilibrium conditions, and did not consider redox potential or metal competition for the adsorption sites. In addition to these constraints, EPA (1996) noted that this approach was limited by the potential sorbent surfaces that could be considered and availability of thermodynamic data. Their calculations were limited to metal adsorption on iron oxide, although sorption of these metals to other minerals, such as clays and carbonates, is well known.

Typically, the data required to derive the values of adsorption parameters that are needed as input for adsorption submodels in chemical reaction codes are more extensive than information reported in a typical laboratory batch K_d study. If the appropriate data are reported, it is likely that a user could hand calculate a composition-based K_d value from the data reported in the adsorption study without the need of a chemical reaction model.

Chemical reaction models can be used, however, to support evaluations of K_d values and related contaminant migration and risk assessment modeling predictions. Chemical reaction codes can be used to calculate aqueous complexation to determine the ionic state and composition of the dominant species for a dissolved contaminant present in a soil-water system. This information may in turn be used to substantiate the conceptual model being used for calculating the adsorption of a particular contaminant. Chemical reaction models can be used to predict bounding, technically defensible maximum concentration limits for contaminants as a function of key composition parameters (*e.g.*, pH) for any specific soil-water system. These values may provide more realistic bounding values for the maximum concentration attainable in a soil-water system when doing risk assessment calculations. Chemical reaction models can also be used to analyze initial and final geochemical conditions associated with laboratory K_d measurements to determine if the measurement had been affected by processes such as mineral precipitation which might have compromised the derived K_d values. Although chemical reaction models cannot be used to predict K_d values, they can provide aqueous speciation and solubility information that is exceedingly valuable in the evaluation of K_d values selected from the literature and/or measured in the laboratory.